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Santra [US/US]; 1905 West Walnut, Duncan, OK 73533 (US).

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(74) Agents: **WAIN, Christopher, Paul et al.**; A A Thornton & Co, 235 High Holborn, London WC1V 7LE (GB).

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(71) Applicant (*for all designated States except US*): **HAL-LIBURTON ENERGY SERVICES, INC.** [US/US]; P.O. Box 1431, Duncan, OK 73533 (US).

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(71) Applicant (*for MW only*): **WAIN, Christopher, Paul** [GB/GB]; A.A. Thornton & Co., 235 High Holborn, London WC1V 7LE (GB).

(72) Inventors; and

Published:

(75) Inventors/Applicants (*for US only*): **LUKE, Karen** [US/US]; 1403 N. 12th, Duncan, OK 73533 (US). **FITZGERALD, Russell, M.** [US/US]; 310 Main, Velma, OK 73491 (US). **ZAMORA, Frank** [US/US]; 2017 Woodcrest Drive, Duncan, OK 73533 (US). **ASHOK, K.,**

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(54) Title: ZEOLITE-CONTAINING SETTABLE SPOTTING FLUIDS

(57) Abstract: Methods and compositions for wellbore treating fluids, especially settable spotting fluids, that include zeolite and at least one carrier fluid.

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## **Zeolite-Containing Settable Spotting Fluids**

### **Background**

The present embodiments relate generally to wellbore treating fluids introduced into a subterranean zone penetrated by a wellbore, particularly wellbore treating fluids introduced as settable spotting fluids.

Conventionally, a wellbore is drilled using a drilling fluid that is continuously circulated down a drill pipe, through a drill bit, and upwardly through the wellbore to the surface. Typically, after a wellbore has been drilled to total depth, the drill bit is withdrawn from the wellbore, and circulation of the drilling fluid is stopped, thereby initiating a shutdown period. During the shutdown period, the drilling fluid is typically left in the wellbore, and a filter cake of solids from the drilling fluid, and additional dehydrated drilling fluid and gelled drilling fluid, typically forms on the walls of the wellbore.

The next operation in completing the wellbore usually involves running a pipe string, e.g., casing, into the wellbore. While the pipe is being run, the drilling fluid left in the wellbore remains relatively static. During that time, the stagnant drilling fluid progressively increases in gel strength, whereby portions of the drilling fluid in the wellbore can become increasingly difficult to displace during subsequent clean-up operations.

After the pipe is run in the wellbore, the next operation typically involves cleaning out the wellbore, which may be accomplished by re-initiating circulation of drilling fluid. The drilling fluid is circulated downwardly through the interior of the pipe and upwardly through the annulus between the exterior of the pipe and the walls of the wellbore, while removing drilling solids, gas, filter cake, dehydrated drilling fluid, gelled drilling fluid, and any other undesired substances needing to be removed from the wellbore.

After clean-up operations are performed in the wellbore, primary cementing operations are typically performed therein. Namely, the pipe is cemented in the wellbore by placing a cement slurry in the annulus between the pipe and the walls of the wellbore. The cement slurry sets into a hard impermeable mass, and is intended to bond the pipe to the walls of the wellbore whereby the annulus is sealed and fluid communication between subterranean zones or to the surface by way of the annulus is prevented.

During any of the above or other operations performed in the wellbore, a number of problems can occur, including difficulty in removing portions of the drilling fluid, or inability

to achieve a satisfactory bond between the pipe and the walls of the wellbore because of drilling fluid that remained in the wellbore during primary cementing operations.

Difficulty in removing portions of the drilling fluid is often caused by an increase in the gel strength of the drilling fluid, which is often due to the amount of time the drilling fluid has been left stagnant in the wellbore. In addition, polymeric viscosifiers and additives in the drilling fluid contribute to the formation of a filter cake that is generally very stable and can be difficult to remove. If appreciable drilling fluid and/or filter cake remain in the wellbore or on the walls of the wellbore, a satisfactory bond between the pipe, primary cement and the walls of the wellbore will not be achieved, which can lead to fluid leakage through the annulus and other problems.

Removal of the drilling fluid and filter cake from the wellbore is often attempted by running flushes, washes or spacer fluids through the annulus between the pipe and the walls of the wellbore prior to cementing. Other methods for removing drilling fluid and preventing filter cake from interfering with subsequent primary cementing operations include at least partially displacing the drilling fluid with a settable spotting fluid composition (also referred to as a "settable spotting fluid") before the drilling fluid in the wellbore has had a chance to gain significant gel strength. Conventional settable spotting fluids include a material that sets over time, such as blast furnace slag, fly ash, and similar hydraulic components. Still other methods for achieving satisfactory primary cementing operations when deposits of filter cake are an issue include laying down a filter cake including a settable material on the walls of the wellbore and activating the settable material to set.

The present embodiments provide wellbore treating fluids in the form of settable spotting fluids that include zeolite as a settable material, and methods for causing the zeolite to set and using such settable spotting fluids in drilling operations.

### **Description**

According to embodiments described herein, wellbore treating fluids comprising zeolite are introduced into a wellbore in the form of a settable spotting fluid.

Methods according to the present embodiments provide for introducing a wellbore treating fluid comprising zeolite into a wellbore penetrating a subterranean zone, introducing a subsequent composition comprising a compressive strength-developing amount of an activator into the wellbore to displace all but a remaining portion of the wellbore treating

fluid from the wellbore, contacting the zeolite in the remaining portion of the wellbore treating fluid with the activator, and allowing the zeolite to set.

Other methods according to the present embodiments provide for introducing a wellbore treating fluid comprising zeolite, a compressive strength-developing amount of an activator, and a retarder, into a wellbore penetrating a subterranean zone, introducing a subsequent composition into the wellbore to displace all but a remaining portion of the wellbore treating fluid from the wellbore, and allowing the zeolite in the remaining portion of the wellbore treating fluid to set.

Setting of the zeolite according to the present embodiments is similar to the setting of settable materials in conventional settable spotting fluids, that is, the zeolite sets into a relatively hard mass. The compressive strength of the set mass formed by the zeolite can be measured and compared to compressive strengths of set materials in conventional settable spotting fluids.

In practicing methods according to the present embodiments, drilling fluid (also referred to herein as "mud") remaining in a wellbore during a shutdown period is at least partially displaced with a settable spotting fluid comprising zeolite. Preferably, the mud in the wellbore is displaced with the settable spotting fluid before the mud has had a chance to gain significant gel strength. By displacing the mud before it gains significant gel strength, difficulties with removing portions of it during clean-up operations in the wellbore are reduced. As used herein, the term "mud" encompasses any fluid used in hydrocarbon drilling operations, including but not limited to all types of water-base, oil-base and synthetic-base drilling fluids, and fluids that contain significant amounts of suspended solids, emulsified water or oil.

According to one embodiment where a settable spotting fluid comprising zeolite at least partially displaces mud from the wellbore, the settable spotting fluid is subsequently flushed out of the wellbore by washes or spacer fluids circulated through the wellbore. A cement slurry may then be pumped into the annulus and allowed to set, thus bonding the pipe to the walls of the wellbore. The setting of the cement, and consequently the bonding of the pipe to the walls of the wellbore, is improved because difficulties with removing portions of the mud from the wellbore are reduced.

According to another embodiment where a settable spotting fluid comprising zeolite

at least partially displaces mud from a wellbore, portions of the settable spotting fluid remain on the walls of the wellbore as part of the filter cake, and/or in permeable areas affecting the wellbore, such as fissures, fractures, caverns, vugs, thief zones, low pressure subterranean zones or high pressure subterranean zones, even if washes or spacer fluids are introduced into the wellbore subsequent to the settable spotting fluid. According to such an embodiment, a subsequent composition, for example, a drilling fluid, pill, spotting fluid or other mud, which contains at least one activator, is pumped into the wellbore. The subsequent composition is pumped into the wellbore, either after the settable spotting fluid, or after the washes or spacer fluids, if such are used. When the activator in the subsequent composition contacts the settable spotting fluid remaining in the filter cake and/or permeable areas, the activator causes the zeolite therein to set. The activator is present in the subsequent composition in a compressive strength-developing amount, and may be one or more of calcium hydroxide, sodium silicate, sodium fluoride, sodium silicofluoride, magnesium silicofluoride, zinc silicofluoride, sodium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, sodium sulfate, and mixtures thereof. Selection of the type and amount of an activator(s) largely depends on the type and make-up of the composition in which the activator is contained, and it is within the means of those of ordinary skill in the art to select a suitable type and amount of activator.

According to yet another embodiment where portions of a settable spotting fluid comprising zeolite remain on the walls of the wellbore as part of the filter cake, and/or in permeable areas affecting the wellbore, primary cementing operations are performed by introducing a cement slurry containing at least one activator into the wellbore. The cement slurry can be introduced after the settable spotting fluid to displace the settable spotting fluid from the wellbore, or can be introduced after a wash or spacer fluid that was pumped into the wellbore after the settable spotting fluid. As the cement slurry is pumped, and as it begins to set in the wellbore, the activator therein diffuses into the settable spotting fluid remaining in the filter cake and/or permeable areas, and causes the zeolite to set. The activator is present in the cement slurry in a compressive strength-developing amount, and may be one or more of calcium hydroxide, sodium silicate, sodium fluoride, sodium silicofluoride, magnesium silicofluoride, zinc silicofluoride, sodium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, sodium sulfate, and mixtures thereof. Selection of the type and amount

of an activator(s) largely depends on the nature and composition of the cement slurry, and it is within the means of those of ordinary skill in the art to select a suitable type and amount of activator.

According to yet another embodiment, a settable spotting fluid comprising zeolite, a compressive strength-developing amount of at least one activator and at least one retarder is introduced into a wellbore. Portions of the settable spotting fluid remain on the walls of the wellbore as part of the filter cake, and/or in permeable areas affecting the wellbore, even if washes or spacer fluids are introduced into the wellbore subsequent to the settable spotting fluid. The activator in the settable spotting fluid causes the zeolite in the remaining portions to set, while the retarder slows the set so that it occurs over a desired period of time.

According to such an embodiment, other drilling operations can proceed, which operations may require other muds, fluids, or compositions to be subsequently pumped into the wellbore. If subsequent muds, fluids, or compositions are pumped into the wellbore, they may or may not comprise an activator. As above, the activator in the settable spotting fluid may be one or more of calcium hydroxide, sodium silicate, sodium fluoride, sodium silicofluoride, magnesium silicofluoride, zinc silicofluoride, sodium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, sodium sulfate, and mixtures thereof. Suitable retarders include but are not limited to one or more of a lignosulfonate, an organic acid having an  $\alpha$ -hydroxy group such as citric acid, tartaric acid or gluconic acid, and combinations of both lignosulfonate and organic acid having an  $\alpha$ -hydroxy group.

Selection of the type and amount of activator(s) and retarder(s) largely depends on the nature and composition of the settable spotting fluid, and it is within the means of those of ordinary skill in the art to select a suitable type and amount of activator and retarder. Moreover, it is within the means of those of ordinary skill in the art to exert control over the amount of time that it takes the zeolite to set by determining, through the exercise of routine experimentation, the amount of retarder necessary to achieve a set over a desired period of time.

Thus, in addition to reducing difficulties with removing drilling fluid during clean-up operations, a settable spotting fluid comprising zeolite also provides a method by which zeolite remaining in the wellbore after displacement of the settable spotting fluid can be caused to set. Zeolite that sets in permeable areas affecting the wellbore, such as fissures,

fractures, caverns, vugs, thief zones, low pressure subterranean zones or high pressure subterranean zones effectively seals such permeable areas, thereby preventing the entry or flow of formation fluids into the annulus.

Zeolites are porous alumino-silicate minerals that may be either a natural or manmade material. Manmade zeolites are based on the same type of structural cell as natural zeolites, and are composed of aluminosilicate hydrates having the same basic formula as given below. It is understood that as used in this application, the term "zeolite" means and encompasses all natural and manmade forms of zeolites. All zeolites are composed of a three-dimensional framework of  $\text{SiO}_4$  and  $\text{AlO}_4$  in a tetrahedron, which creates a very high surface area. Cations and water molecules are entrained into the framework. Thus, all zeolites may be represented by the crystallographic unit cell formula:



where M represents one or more cations such as Na, K, Mg, Ca, Sr, Li or Ba for natural zeolites and  $\text{NH}_4$ ,  $\text{CH}_3\text{NH}_3$ ,  $(\text{CH}_3)_3\text{NH}$ ,  $(\text{CH}_3)_4\text{N}$ , Ga, Ge and P for manmade zeolites; n represents the cation valence; the ratio of b:a is in a range from greater than or equal to 1 and less than or equal to 5; and x represents the moles of water entrained into the zeolite framework.

Preferred zeolites for use in the wellbore treating fluids of the present embodiments include analcime (hydrated sodium aluminum silicate), bikitaite (lithium aluminum silicate), brewsterite (hydrated strontium barium calcium aluminum silicate), chabazite (hydrated calcium aluminum silicate), clinoptilolite (hydrated sodium aluminum silicate), faujasite (hydrated sodium potassium calcium magnesium aluminum silicate), harmotome (hydrated barium aluminum silicate), heulandite (hydrated sodium calcium aluminum silicate), laumontite (hydrated calcium aluminum silicate), mesolite (hydrated sodium calcium aluminum silicate), natrolite (hydrated sodium aluminum silicate), paulingite (hydrated potassium sodium calcium barium aluminum silicate), phillipsite (hydrated potassium sodium calcium aluminum silicate), scolecite (hydrated calcium aluminum silicate), stellerite (hydrated calcium aluminum silicate), stilbite (hydrated sodium calcium aluminum silicate) and thomsonite (hydrated sodium calcium aluminum silicate). Most preferably, the zeolites for use in the wellbore treating fluids of the present embodiment include chabazite and clinoptilolite.

Carrier fluids suitable for use in the embodiments of wellbore treating fluids, such as settable spotting fluids disclosed herein, comprise aqueous fluids, oil-based and synthetic-based fluids, emulsion, acids, or mixtures thereof. Exemplary aqueous fluids include but are not limited to water and water-based gels. When the carrier fluid comprises water, the water can be fresh water, unsaturated salt solution, including brines and seawater, and saturated salt solution. Exemplary oil-based fluids include but are not limited to canola oil, kerosene, diesel oil, fish oil, mineral oil, sunflower oil, corn oil, soy oil, olive oil, cottonseed oil, peanut oil and paraffin. Exemplary synthetic-based fluids include but are not limited to esters, olefins and ethers. The preferred carrier fluid for the wellbore treating fluid comprising zeolite as disclosed herein depends upon the properties desired for the wellbore treating fluid, as well as the cost, availability, temperature, stability, viscosity, clarity, and the like of the carrier fluid.

According to one embodiment, a settable spotting fluid comprising zeolite is prepared by mixing an amount of zeolite with a carrier fluid in an amount of from about 100 to about 200 weight percent, based on the weight of the amount of zeolite. According to embodiments where a settable spotting fluid comprising zeolite at least partially displaces a mud, the mud can be a water-based drilling fluid, an oil-based drilling fluid, or a synthetic-based drilling fluid.

In carrying out the methods of the present embodiments, a wellbore treating fluid comprising zeolite and at least one carrier fluid is introduced into a wellbore to at least partially displace a mud from the wellbore. A subsequent composition is introduced into the wellbore to displace all but a remaining portion of the wellbore treating fluid from the wellbore. The zeolite in the remaining portion of the wellbore treating fluid sets into a relatively hard mass. Displacement of the mud from the wellbore and setting of zeolite remaining in the wellbore contribute to the creation of satisfactory conditions for primary cementing operations. In addition, setting of zeolite that remained in one or more permeable areas affecting the wellbore, such as fissures, fractures, caverns, vugs, thief zones, low pressure subterranean zones or high pressure subterranean zones effectively seals such permeable areas, thereby preventing the entry or flow of formation fluids into the annulus.

The following examples are illustrative of the foregoing methods and compositions.



**EXAMPLE 1**

Six settable spotting fluids ("Spots") were prepared by combining the components as set forth in **TABLE 1** below. Specifically, the zeolite and the hydrated lime were dry-mixed by hand in a glass jar. This dry mix was then added over a 15 second period to a carrier fluid being maintained in a Waring blender at 4,000 RPM. The blender speed was then increased to 12,000 RPM and mixing was continued for 35 seconds.

According to the embodiments illustrated in Table 1, the carrier fluid was water. The amount of hydrated lime and water used to form each settable spotting fluid is reported in the table as a "% bwoZ", which indicates a weight percent based on the weight of the zeolite.

Chabazite was used as the zeolite for Spots 1 – 4, and clinoptilolite was used as the zeolite for Spots 5 – 6. Each of these zeolites is commercially available from C2C Zeolite Corporation of Calgary, Canada.

The compressive strength for each of Spots 1 – 6 was determined by Non-Destructive Sonic Testing as set forth in API Specification 10B 22nd Edition, 1997, of the American Petroleum Institute, the entire disclosure of which is incorporated herein by reference as if reproduced in its entirety. As reported in Table 1, the compressive strength was measured at 160°F at the reported elapsed times. The measured compressive strength is reported in Table 1 in pounds per square inch (psi).

TABLE 1

	Spot 1	Spot 2	Spot 3	Spot 4	Spot 5	Spot 6
<b>Components</b>						
Zeolite (chabazite) wt. %	100	100	100	100	0	0
Zeolite (clinoptilolite) wt. %	0	0	0	0	100	100
Hydrated Lime (%bwoZ)	7	10	15	35	15	35
Water (% bwoZ)	106	109	114	136	114	136
	<b>Spot 1</b>	<b>Spot 2</b>	<b>Spot 3</b>	<b>Spot 4</b>	<b>Spot 5</b>	<b>Spot 6</b>
<b>Compressive Strength (psi) Measured at 160 °F and at Time</b>						
Time: 4 Hr	0	280	500	500	250	250
Time: 8 Hr	0	290	540	700	340	440
Time: 12 Hr	0	290	568	730	350	530
Time: 24 Hr	0	290	568	750	374	590

The compressive strength data indicates that wellbore treating fluids comprising zeolite and water, such as the settable spotting fluids illustrated in Example 1, develop compressive strengths when the amount of an activator, such as lime, is present in an amount greater than about 7% based on the weight of the zeolite. The identity of the activator, zeolite, and carrier fluid may influence the amount of activator necessary to cause the settable spotting fluid to set; thus, in some embodiments, the settable spotting fluid may develop compressive strength with activator amounts less than the 7% illustrated by Example 1. Accordingly, the amount of activator used in practicing the present embodiments need only be at least a compressive strength-developing amount. Those of ordinary skill in the art can determine through the exercise of routine experimentation the amount of an activator sufficient for the development of compressive strength.

The compressive strength data also indicates that wellbore treating fluids comprising zeolite and water, such as the settable spotting fluids of Spots 2 – 6, develop compressive strengths that are suitable for use with wellbore applications in which conventional settable

spotting fluids are used.

The compressive strength data also illustrates that settable spotting fluids comprising zeolite and water develop an early compressive strength, which increases over time. This illustrates that the zeolite will set, and is a satisfactory substitute for settable material, such as blast furnace slag, fly ash and other hydraulic materials, used in conventional settable spotting fluids. In the settable spotting fluids of Example 1, setting of the zeolite was caused by the lime, also known as calcium hydroxide, which is a known activator for converting settable material in conventional settable spotting fluids. Thus, when an activator, such as lime, is brought into contact with a wellbore treating fluid comprising zeolite, such as the settable spotting fluids illustrated herein, the activator causes the zeolite to set.

Contact between an activator and a settable material can be accomplished by various methods well known to those of ordinary skill in the art. The addition of the lime and zeolite together in a settable spotting fluid as described in this example simulates two of the various methods suitable for bringing an activator into contact with the zeolite. According to the first method simulated by this example, zeolite from wellbore treating fluids, such as the settable spotting fluids illustrated herein, remains on the walls of the wellbore as part of the filter cake, and/or in permeable areas affecting the wellbore, such as fissures, fractures, caverns, vugs, thief zones, low pressure subterranean zones or high pressure subterranean zones, even if subsequent washes or spacer fluids are used to displace the wellbore treating fluid. An activator is brought into contact with the zeolite remaining in the wellbore by circulation of a subsequent composition, such as a drilling fluid, pill, spotting fluid or other mud, which contains the activator. According to the second method simulated by this example, an activator is brought into contact with the zeolite remaining in the wellbore by diffusion of an activator contained in a cement slurry that is subsequently pumped into the wellbore during primary cementing operations.

The two methods simulated by this example are exemplary only, as a variety of methods for bringing a settable material into contact with an activator, which are well known to those of ordinary skill in the art, are suitable for use with the present embodiments. Example 2 illustrates yet another method.

**Example 2**

Three settable spotting fluids (Spots 1, 2, and 3) were prepared by combining the components as set forth in TABLE 2A below. Specifically, the zeolite, hydrated lime, and retarder were dry-mixed by hand in a glass jar. This dry mix was then added over a 15 second period to a carrier fluid being maintained in a Waring blender at 4,000 RPM. The blender speed was then increased to 12,000 RPM and mixing was continued for 35 seconds.

According to the embodiment illustrated in Table 2A, the carrier fluid was water. The amount of hydrated lime, retarder and water used to form the settable spotting fluid is reported in the table as a "% bwoZ", which indicates a weight percent based on the weight of the zeolite. chabazite, which is commercially available from C2C Zeolite Corporation of Calgary, Canada, was used as the zeolite. The retarder comprised a 2/1 lignosulfonate/tartaric acid solution, which is commercially available under the tradename HR-13L from Halliburton Energy Services, Duncan, Oklahoma.

**TABLE 2A**

<b>Components</b>	<b>Spot 1</b>	<b>Spot 2</b>	<b>Spot 3</b>
Zeolite (wt. %) (chabazite)	100	100	100
Hydrated Lime (% bwoZ)	15	15	15
Retarder (HR-13 L) (% bwoZ)	3.2	3.2	3.6
Water (% bwoZ)	97.64	97.64	97.64

The strengths of each of Spots 1, 2 and 3 were then tested at the temperatures and times reported in Table 2B. Up to Day 3, each of Spots 1, 2 and 3 were gelatinous. Thus, the gel strength of each of Spots 1, 2 and 3 was measured according to API Recommended Practice Standard Procedure for Field Testing Drilling Fluids 13B, Appendix B, Shear Strength Measurement using Shearometer Tube, the entire disclosure of which is incorporated herein by reference. The test was performed using a Fann® Model 240 Shearometer, available from Fann Instrument Company, Houston, Texas, and operated according to the Fann® Model 240 Shearometer Instruction Card, the entire disclosure of which is incorporated herein by reference. The gel strength of each of Spots 1, 2 and 3 are reported in Table 2A in pounds per 100 square feet of area ("lb/100 ft<sup>2</sup>").

After Spots 1, 2 and 3 turned from gelatinous to solid, the compressive strengths at

Days 5 and 6 as reported in Table 2B were determined. The compressive strengths are reported in Table 2B in pounds per square inch ("psi"). To determine the compressive strength, each of Spots 1, 2 and 3 were placed in sealed cylindrical plastic containers, 2 inches in diameter by 4 inches in height. Each plastic container was placed in a water bath at the temperature reported in Table 2B, under atmospheric pressure, for the time periods reported in Table 2B. Each plastic container was then removed from the water bath, allowed to cool, and the cylindrical samples were demolded. The top end of each cylindrical sample was cut using a tile saw to give a smooth and level surface. The remainder of the sample was then placed in a Tinius Olsen universal testing machine and the compressive strength determined according to operating procedures for the universal testing machine.

**TABLE 2B**

<b>Gel Strength and Compressive Strength Measured at Temp °F and at Time</b>						
<b>Spot #: Test Temp.</b>	<b>Time Day 1</b>	<b>Time Day 2</b>	<b>Time Day 3</b>	<b>Time Day 4</b>	<b>Time Day 5</b>	<b>Time Day 6</b>
<b>Spot 1: Temp: 140 °F</b>	< 10 lb/100 ft <sup>2</sup>	< 10 lb/100 ft <sup>2</sup>	< 10 lb/100 ft <sup>2</sup>	~ 100 lb/100 ft <sup>2</sup>	gel turned to solid	> 250 psi
<b>Spot 2: Temp: 160 °F</b>	< 10 lb/100 ft <sup>2</sup>	< 10 lb/100 ft <sup>2</sup>	< 10 lb/100 ft <sup>2</sup>	gel turned to solid	> 280 psi	not taken
<b>Spot 3: Temp: 190 °F</b>	< 10 lb/100 ft <sup>2</sup>	< 10 lb/100 ft <sup>2</sup>	< 10 lb/100 ft <sup>2</sup>	~ 100 lb/100 ft <sup>2</sup>	gel turned to solid	> 230 psi

The gel strength and compressive strength data indicates that wellbore treating fluids

comprising zeolite, water, at least one activator and at least one retarder, such as the settable spotting fluid illustrated in Table 2A, develop strength over time at a range of temperatures. This illustrates that the zeolite will set, and is a satisfactory substitute for settable material, such as blast furnace slag, fly ash and other hydraulic materials, used in conventional settable spotting fluids. The identity of the activator(s), zeolite, retarder(s) and carrier fluid(s) may influence the amount of activator necessary to cause the settable spotting fluid to set, as well as the amount of retarder necessary to slow the set. Accordingly, the amount of activator used in practicing the present embodiments is described as a compressive strength-developing amount. Moreover, the amount of retarder can be adjusted up or down to control the amount of time it takes for the settable spotting fluid to develop strength. Those of ordinary skill in the art can determine a desirable time to achieve a set, and through the exercise of routine experimentation, determine the amount of retarder necessary to achieve a set over the desired period of time. Accordingly, the amounts of activator, zeolite, retarder and carrier fluid as listed in Example 2 are merely an exemplary embodiment.

In the settable spotting fluid illustrated in Example 2, the activator (i.e., the lime) caused the zeolite to set, while the retarder slowed the set so that setting occurred over time. This illustrates yet another method for bringing an activator into contact with the zeolite in portions of settable spotting fluid that remains in the wellbore.

Moreover, the present embodiments provide a method for performing drilling operations wherein a wellbore treating fluid comprising zeolite, such as the settable spotting fluids illustrated by Examples 1 and 2, at least partially displaces a mud used to drill a wellbore. Preferably, the mud is displaced by the settable spotting fluid comprising zeolite before the mud has had an opportunity to develop a gel strength significant enough to make its displacement difficult. After the mud is at least partially displaced by the settable spotting fluid, a cement slurry may then be pumped into the annulus. The cement slurry is allowed to set, thus bonding the pipe to the walls of the wellbore. The setting of the cement, and consequently the bonding of the pipe to the walls of the wellbore, is improved because difficulties with removing portions of the drilling fluid in the wellbore are reduced.

While the embodiments described herein relate to wellbore treating fluids provided as settable spotting fluids, it is understood that any wellbore treating fluids such as drilling, completion and stimulation fluids including, but not limited to, drilling muds, cement

compositions, remedial compositions, well cleanup fluids, workover fluids, spacer fluids, gravel pack fluids, acidizing fluids, fracturing fluids, conformance fluids and the like can be prepared using zeolite and a carrier fluid. Accordingly, improved methods of the present invention comprise preparing a wellbore treating fluid using at least one carrier fluid and zeolite, as previously described herein, and placing the fluid in a subterranean formation. Other methods according to the present embodiments include performing drilling operations, completing and/or stimulating a subterranean formation, and performing primary cementing operations using a wellbore treating fluid comprising zeolite and at least one carrier fluid.

Other embodiments of the current invention will be apparent to those skilled in the art from a consideration of this specification or practice of the invention disclosed herein. However, the foregoing specification is considered merely exemplary of the current invention with the true scope and spirit of the invention being indicated by the following claims.

**What is claimed is:**

1. A method of performing drilling operations comprising the steps of:  
penetrating a subterranean zone with a wellbore;  
introducing a wellbore treating fluid comprising zeolite and at least one carrier fluid into the wellbore;  
introducing a subsequent composition comprising a compressive strength-developing amount of at least one activator into the wellbore to displace all but a remaining portion of the wellbore treating fluid from the wellbore; and  
contacting the zeolite in the remaining portion of the wellbore treating fluid with the at least one activator.
2. The method of claim 1 further comprising:  
allowing the zeolite in the remaining portion of the wellbore treating fluid to set.
3. The method of claim 1 wherein the remaining portion of the wellbore treating fluid is in one or more of a filter cake, fissure, fracture, cavern, vug, thief zone, low pressure subterranean zone, and high pressure subterranean zone in the wellbore.
4. The method of claim 3 further comprising:  
allowing the zeolite in the remaining portion of the wellbore treating fluid to set, wherein the set zeolite seals one or more of a fissure, fracture, cavern, vug, thief zone, low pressure subterranean zone, and high pressure subterranean zone in the wellbore.
5. The method of claim 1 wherein the penetrating of the subterranean zone with a wellbore comprises drilling the wellbore with a mud, and wherein the introducing of the wellbore treating fluid at least partially displaces the mud from the wellbore.
6. The method of claim 1 wherein the introducing of the subsequent composition comprises:  
introducing a drilling fluid comprising a compressive strength-developing amount of at least one activator into the wellbore.
7. The method of claim 6 wherein the at least one activator is selected from the group consisting of calcium hydroxide, sodium silicate, sodium fluoride, sodium silicofluoride, magnesium silicofluoride, zinc silicofluoride, sodium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, sodium sulfate, and mixtures thereof.
8. The method of claim 6 further comprising placing a cement slurry in the wellbore



after the introducing of the drilling fluid.

9. The method of claim 1 wherein the introducing of the subsequent composition comprises:

introducing a cement slurry comprising a compressive strength-developing amount of at least one activator into the wellbore; and

allowing the at least one activator to diffuse into contact with the zeolite in the remaining portion of the wellbore treating fluid.

10. The method of claim 9 wherein the at least one activator is selected from the group consisting of calcium hydroxide, sodium silicate, sodium fluoride, sodium silicofluoride, magnesium silicofluoride, zinc silicofluoride, sodium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, sodium sulfate, and mixtures thereof.

11. The method of claim 1 wherein the introducing of the subsequent composition comprises:

introducing at least one of a mud, a spotting fluid, a pill and a cement slurry comprising a compressive strength-developing amount of at least one activator into the wellbore.

12. The method of claim 11 wherein the at least one activator is selected from the group consisting of calcium hydroxide, sodium silicate, sodium fluoride, sodium silicofluoride, magnesium silicofluoride, zinc silicofluoride, sodium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, sodium sulfate, and mixtures thereof.

13. The method of claim 1 wherein the zeolite is represented by the formula:



where M represents one or more cations selected from the group consisting of Na, K, Mg, Ca, Sr, Li, Ba,  $NH_4$ ,  $CH_3NH_3$ ,  $(CH_3)_3NH$ ,  $(CH_3)_4N$ , Ga, Ge and P; n represents the cation valence; the ratio of b:a is in a range from greater than or equal to 1 and less than or equal to 5; and x represents the moles of water entrained into the zeolite framework.

14. The method of claim 1, wherein the zeolite is selected from the group consisting of analcime, bikitaite, brewsterite, chabazite, clinoptilolite, faujasite, harmotome, heulandite, laumontite, mesolite, natrolite, paulingite, phillipsite, scolecite, stellerite, stilbite, and thomsonite.

15. The method of claim 1 wherein the at least one carrier fluid comprises a water-based

carrier fluid in an amount of from about 100 to about 200 percent by weight of the zeolite.

16. The method of claim 1 wherein the at least one carrier fluid is selected from the group consisting of water and water-based gels.

17. The method of claim 1 wherein the at least one carrier fluid is selected from the group consisting of fresh water, unsaturated salt solution, brine, seawater, and saturated salt solution.

18. The method of claim 1 wherein the at least one carrier fluid comprises an oil-based fluid selected from the group consisting of canola oil, kerosene, diesel oil, fish oil, mineral oil, sunflower oil, corn oil, soy oil, olive oil, cottonseed oil, peanut oil and paraffin.

19. A method of performing drilling operations comprising the steps of:

penetrating a subterranean zone with a wellbore;

introducing a wellbore treating fluid comprising zeolite, a compressive strength-developing amount of at least one activator, at least one retarder and at least one carrier fluid into the wellbore; and

introducing a subsequent composition into the wellbore to displace all but a remaining portion of the wellbore treating fluid from the wellbore.

20. The method of claim 19 further comprising:

allowing the zeolite in the remaining portion of the wellbore treating fluid to set.

21. The method of claim 19 wherein the remaining portion of the wellbore treating fluid is in one or more of a filter cake, fissure, fracture, cavern, vug, thief zone, low pressure subterranean zone, and high pressure subterranean zone in the wellbore.

22. The method of claim 21 further comprising:

allowing the zeolite in the remaining portion of the wellbore treating fluid to set, wherein the set zeolite seals one or more of a fissure, fracture, cavern, vug, thief zone, low pressure subterranean zone, and high pressure subterranean zone in the wellbore.

23. The method of claim 19 wherein the penetrating of the subterranean zone with a wellbore comprises drilling the wellbore with a mud, and wherein the introducing of the wellbore treating fluid at least partially displaces the mud from the wellbore.

24. The method of claim 19 wherein the at least one activator is selected from the group consisting of calcium hydroxide, sodium silicate, sodium fluoride, sodium silicofluoride, magnesium silicofluoride, zinc silicofluoride, sodium carbonate, potassium carbonate,

sodium hydroxide, potassium hydroxide, sodium sulfate, and mixtures thereof.

25. The method of claim 19 wherein the at least one retarder is selected from the group consisting of lignosulfonates, citric acids, tartaric acids, gluconic acids, organic acids having an  $\alpha$ -hydroxy group, and combinations thereof.
26. The method of claim 19 further comprising placing a cement slurry in the wellbore after the introducing of the subsequent composition.
27. The method of claim 19 wherein the introducing of the subsequent composition comprises introducing at least one of a mud, a spotting fluid, a pill and a cement slurry into the wellbore.
28. The method of claim 27 wherein the subsequent composition comprises at least one activator.
29. The method of claim 28 wherein the at least one activator is selected from the group consisting of calcium hydroxide, sodium silicate, sodium fluoride, sodium silicofluoride, magnesium silicofluoride, zinc silicofluoride, sodium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, sodium sulfate, and mixtures thereof.
30. The method of claim 19 wherein the zeolite is represented by the formula:
 
$$M_{a/n}[(AlO_2)_a(SiO_2)_b] \cdot xH_2O$$
 where M represents one or more cations selected from the group consisting of Na, K, Mg, Ca, Sr, Li, Ba,  $NH_4$ ,  $CH_3NH_3$ ,  $(CH_3)_3NH$ ,  $(CH_3)_4N$ , Ga, Ge and P; n represents the cation valence; the ratio of b:a is in a range from greater than or equal to 1 and less than or equal to 5; and x represents the moles of water entrained into the zeolite framework.
31. The method of claim 19 wherein the zeolite is selected from the group consisting of analcime, bikitaite, brewsterite, chabazite, clinoptilolite, faujasite, harmotome, heulandite, laumontite, mesolite, natrolite, paulingite, phillipsite, scolecite, stellerite, stilbite, and thomsonite.
32. The method of claim 19 wherein the at least one carrier fluid comprises a water-based carrier fluid in an amount of from about 100 to about 200 percent by weight of the zeolite.
33. The method of claim 19 wherein the at least one carrier fluid is selected from the group consisting of water and water-based gels.
34. The method of claim 19 wherein the at least one carrier fluid is selected from the group consisting of fresh water, unsaturated salt solution, brine, seawater, and saturated salt

solution.

35. The method of claim 19 wherein the at least one carrier fluid comprises an oil-based fluid selected from the group consisting of canola oil, kerosene, diesel oil, fish oil, mineral oil, sunflower oil, corn oil, soy oil, olive oil, cottonseed oil, peanut oil and paraffin.

36. A method of performing drilling operations comprising the steps of:

penetrating a subterranean zone with a wellbore;

introducing a wellbore treating fluid comprising zeolite and at least one carrier fluid into the wellbore;

introducing a subsequent composition comprising at least one activator into the wellbore to displace all but a remaining portion of the wellbore treating fluid from the wellbore; and

contacting the zeolite in the remaining portion of the wellbore treating fluid with the at least one activator.

37. A method of performing drilling operations comprising the steps of:

penetrating a subterranean zone with a wellbore;

introducing a wellbore treating fluid comprising zeolite, at least one activator, at least one retarder and at least one carrier fluid into the wellbore; and

introducing a subsequent composition into the wellbore to displace all but a remaining portion of the wellbore treating fluid from the wellbore.

38. A settable spotting fluid comprising zeolite and at least one carrier fluid.

39. The settable spotting fluid of claim 38 wherein the zeolite is represented by the formula:



where M represents one or more cations selected from the group consisting of Na, K, Mg, Ca, Sr, Li, Ba, NH<sub>4</sub>, CH<sub>3</sub>NH<sub>3</sub>, (CH<sub>3</sub>)<sub>3</sub>NH, (CH<sub>3</sub>)<sub>4</sub>N, Ga, Ge and P; n represents the cation valence; the ratio of b:a is in a range from greater than or equal to 1 and less than or equal to 5; and x represents the moles of water entrained into the zeolite framework.

40. The settable spotting fluid of claim 38, wherein the zeolite is selected from the group consisting of analcime, bikitaite, brewsterite, chabazite, clinoptilolite, faujasite, harmotome, heulandite, laumontite, mesolite, natrolite, paulingite, phillipsite, scolecite, stellerite, stilbite, and thomsonite.

41. The settable spotting fluid of claim 38 further comprising at least one activator and at least one retarder.
42. The settable spotting fluid of claim 41 wherein the at least one activator is present in a compressive strength-developing amount.
43. The settable spotting fluid of claim 41 wherein the at least one activator is selected from the group consisting of calcium hydroxide, sodium silicate, sodium fluoride, sodium silicofluoride, magnesium silicofluoride, zinc silicofluoride, sodium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, sodium sulfate, and mixtures thereof.
44. The settable spotting fluid of claim 41 wherein the at least one retarder is selected from the group consisting of lignosulfonates, citric acids, tartaric acids, gluconic acids, organic acids having an  $\alpha$ -hydroxy group, and combinations thereof.
45. The method of claim 38 wherein the at least one carrier fluid comprises a water-based carrier fluid in an amount of from about 100 to about 200 percent by weight of the zeolite.
46. The method of claim 38 wherein the at least one carrier fluid is selected from the group consisting of water and water-based gels.
47. The method of claim 38 wherein the at least one carrier fluid is selected from the group consisting of fresh water, unsaturated salt solution, brine, seawater, and saturated salt solution.
48. The method of claim 38 wherein the at least one carrier fluid comprises an oil-based fluid selected from the group consisting of canola oil, kerosene, diesel oil, fish oil, mineral oil, sunflower oil, corn oil, soy oil, olive oil, cottonseed oil, peanut oil and paraffin.

# INTERNATIONAL SEARCH REPORT

Int'l Application No  
P/ B2004/004899

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 E21B33/13 C04B14/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 E21B C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, COMPENDEX

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	EP 1 428 805 A (HALLIBURTON ENERGY SERVICES, INC) 16 June 2004 (2004-06-16) page 2, line 1 - page 3, line 26; claims 1-12; examples 1-6	1-47
A	US 4 888 120 A (MUELLER ET AL) 19 December 1989 (1989-12-19) column 1, line 48 - column 4, line 43; claims 1-37	1-48
X	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 04, 31 May 1995 (1995-05-31) & JP 07 003254 A (TERUNAITO:KK), 6 January 1995 (1995-01-06) abstract	1, 38

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+31-70) 340-3016

Authorized officer

Wengeler, H

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Original Application No

3B2004/004899

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1428805	A	16-06-2004	US 2004107877 A1	10-06-2004
			CA 2425019 A1	10-06-2004
			EP 1428805 A1	16-06-2004
			US 2004108113 A1	10-06-2004
			US 2004112600 A1	17-06-2004
			US 2004188091 A1	30-09-2004
			US 2005000734 A1	06-01-2005
			US 2004244977 A1	09-12-2004
			US 2004188092 A1	30-09-2004
US 4888120	A	19-12-1989	DE 3631764 A1	24-03-1988
			AT 63132 T	15-05-1991
			BR 8704798 A	17-05-1988
			CA 1296513 C	03-03-1992
			DE 3769735 D1	06-06-1991
			EP 0260538 A2	23-03-1988
			GR 3001896 T3	23-11-1992
			MX 169678 B	19-07-1993
JP 07003254	A	06-01-1995	JP 2957293 B2	04-10-1999

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